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16. Abstract

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THE T-T-T CURVE IN Cu-Cr ALLOY

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Hisashi Suzuki and Motohiro Kanno**

I. Introduction

A considerable amount of studies has been done on Cu-Cr alloys [1]-[5] hardened by aging and in recent years its recovery phenomenon [6,7] ; the time sensitive structures are also being investigated. According to these studies, the GP phase and the intermediate phase do not exist in Cu-Cr alloy and simple homogeneous precipitation is observed. On the other hand, the isothermal transformation curve (T-T-T-curve) was recently investigated [9,10] in connection with the characteristics of quenching of the thick objects. It was reported that the curve possessed two noses and had the ε-shape [10]. This is clearly in contradiction to the C-curve having a single nose which is expected from the past understanding. The cause is suspected to be the difference between homogeneous and heterogeneous precipitations. However, this has not been confirmed so far.

In the present study, therefore, we carried out not only experiments for confirmation of the shape of T-T-T curve, but also experiments for obtaining the pseudo T-T-T curve observed in the conventional water quenching. We found that the curve was of the ε-shape and this was caused from the fact that the type of Cr precipitation varied according to the processing conditions.

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* Numbers in margin indicate pagination of foreign text.

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II. Specimens and experimental method /435

We used copper by electrolysis and Cr-Cu alloy (Cu-5%, Cr alloy) and melted them in the atmosphere under a flux cover, and thus obtained three kinds of Cr-Cu, namely 0.23, 0.70 and 1.16% Cr, respectively. All these specimens were pressed to 3 mm thick between a heat gap (800-900°C). After rinsing in acid, they were cool-pressed to 1 mm thick plates. For obtaining the T-T-T curve, we heat-processed the specimens (isothermal processing) as shown in the first half of Figure 1(a). At point (1) in the figure, we measured the electric conductivity (ρ) and the hardness (Hv). The heat treatment shown in the latter half of Figure 1(a) was also carried out and at point (2), we determined Hv, ΔHv and $\Delta\rho$ and compared the curve with similar curves obtained earlier. We also obtained the pseudo T-T-T curve from the measured values at point (1) and Point (2) in Figure 1(b) where the heat treatment was equivalent to the conventional water quenching. Also, we applied step aging whenever necessary. For structural study, we used 0.5 mm thick specimens. All these specimens were made to thin films by chemical polishing and electrolysis polishing after various heat treatments [8], and the structure was observed by transmission electron micrography.

III. Experimental results

We first studied the shape of the T-T-T curve. For example, if we sought the curve based on measurement of the electric conductivity (ρ) of low and high concentration alloys, we obtained Figures 2 and 3*. We omitted the curve corresponding to the intermediate concentration since it was located between the former two

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*In general, the T-T-T curve consists of the starting line and the finishing line. However, in precipitation, starting and ending of precipitation cannot be shown exactly. Therefore, we determined the shape of the T-T-T curve using the electric conductivities corresponding to equivalent amounts of precipitation.

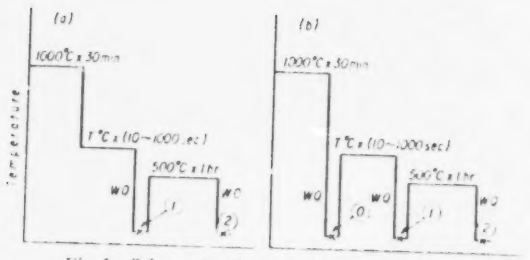

Fig.1 Schematic diagram of heat-treatment

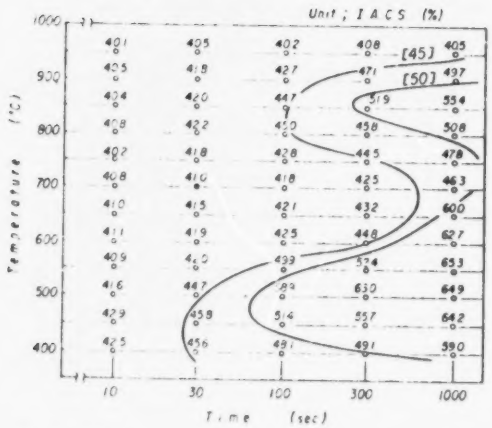

Fig.2 Time temperature-transformation diagram of Cu-0.23% Cr alloy based on electrical conductivity. Refer to Fig.1 (a) - 1

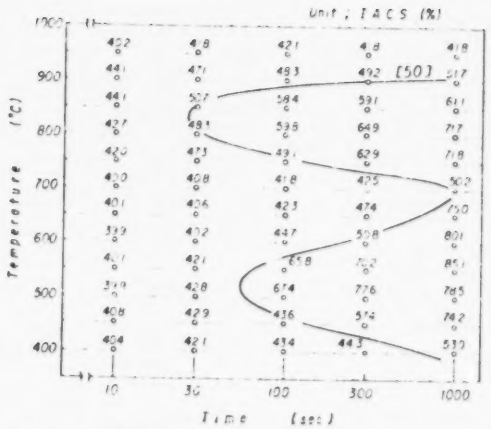

Fig.3 T-T-T diagram of Cu-1.16% Cr alloy based on electrical conductivity. Refer to Fig.1 (a) 1

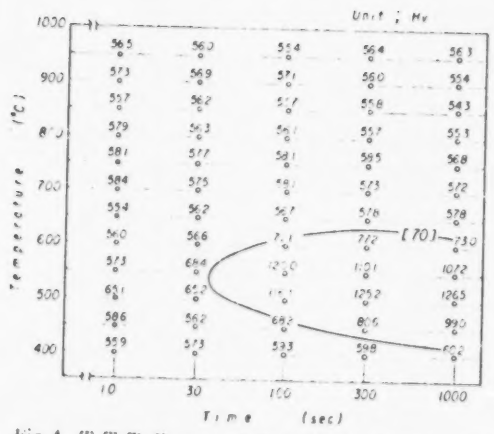

Fig.4 T-T-T diagram of Cu-1.16% Cr alloy based on hardness. Refer to Fig.1 (a) -1

curves. In all cases, the curves have two noses and of the ε-type, independent of the Cr concentration. However, the nose at the higher temperature is more pronounced as the concentration increases. Also, near the low temperature nose, the initial precipitation is faster in alloys of low concentration, but as time elapses, it becomes slower than in the low concentration. Our results more or less agree with the results obtained by Sato, et al. [10]. Thus, we confirmed that the T-T-T curve of Cu-Cr alloy was of the ε-shape.

In Figure 4, we show measured values of the hardness (Hv) corresponding to the above measurements of the electric conductivity in two specimens of high concentration where two noses were very pronounced. In this case, the hardness curve has a nose in the low temperature side, but does not have a nose corresponding to the above described nose in the high temperature side. Variations of the hardness was negligible in this temperature range.

The reason for this hardness being almost invariant even /436
though precipitation has definitely occurred, judging from the change of p is probably that in the high temperature region the distribution of precipitates is extremely inhomogeneous as shown below. However, we can obtain a curve similar to the T-T-T curve from the hardness measurement also. Figure 5 shows measured values of a specimen which, after isothermal treatment, was aged by 500°Cx 1 hr (the commonly used aging treatment for Cr-Cu alloy), and we obtained in this figure a curve similar to that in Figure 3. In the temperature range where precipitation is fast in isothermal treatment, especially near the nose, the hardness decreased considerably because of decrease of the amount of precipitates by the subsequent aging. As mentioned earlier, if treatment is done at high temperatures, the amount of precipitates and the hardness variation do not correspond to each other. Therefore, in Figure 6, we showed the increment ΔHv of the hardness by aging after the isothermal treatment in contrast to Figure 5. This corresponds

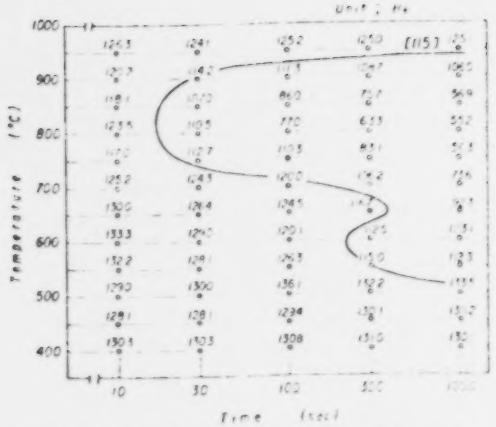

Fig.5 Pseudo T-T-T diagram of Cu-1.16% Cr alloy based on hardness after aging at 500 C for 1 hr. Refer to Fig.1 (c) - 2

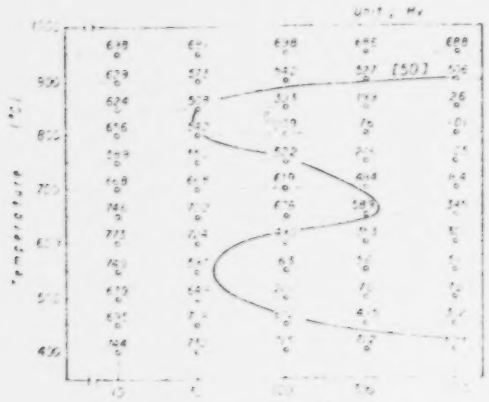

Fig.6 Pseudo T-T-T diagram of Cu-1.16% Cr alloy based on the increment in hardness (ΔHv) by aging at 500 C for 1 hr. Refer to Fig.1 (a) ($\Delta Hv = Hv_{(2)} - Hv_{(1)}$)

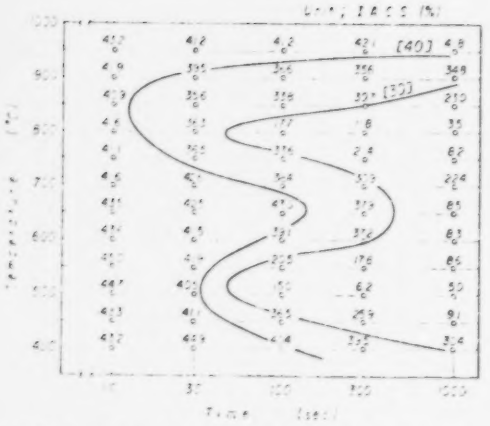

Fig.7 Pseudo T-T-T diagram of Cu-1.16% Cr alloy based on the increment in electrical conductivity ($\Delta\rho$) by subsequent aging. Refer to Fig.1 (b) ($\Delta\rho = \rho_{(2)} - \rho_{(1)}$)

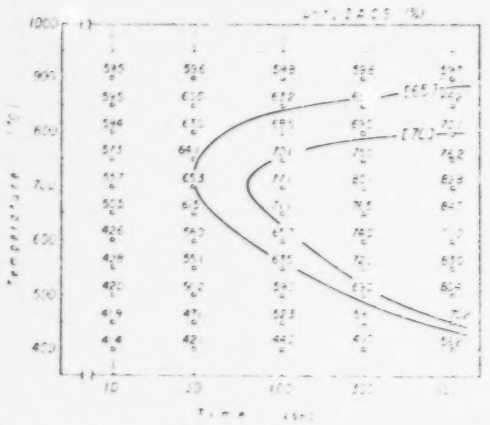

Fig.8 Pseudo T-T-T diagram of quenched Cu-1.16% Cr alloy based on the electrical conductivity. Refer to Fig.1 (b) - 1

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closely to the curve in Figure 7 where the curve of Δp (considered to be approximately proportional to the amount of precipitates) is of the same specimen. The above discussion led us to the conclusion that if we determine p, Δp, ΔHv, etc. in Cr-Cu alloy after the above described isothermal treatment, we obtain the T-T-T curve having two noses and of the ε-shape.

Next, we investigated the pseudo T-T-T curve when the conventional heat treatment (see Figure 1(b),(e) was applied after water quenching. Figure 8 shows the results obtained from measurements of the electric conductivity of a high concentration alloy. According to this figure, a single nose exists near 700°C and two noses do not exist as observed in isothermal treatment (see Figure 3). In the isothermal treatment described earlier, precipitation was very slow at around 700°C and this temperature corresponds to the valley of the curve. However, in water quenching, this temperature is the nose temperature and the precipitation is very fast. Also, the equi-electric conductivity curve shifts considerably towards the side of the short elapsed time, compared to the case of isothermal treatment. Precipitation at each temperature was found to be accelerated in water quenching. We omit presentation of results of hardness /437 variation. However, we obtained results similar to the above C-curve observed in the isothermal treatment, from ΔHv measurements. Also, they remained almost the same even if the concentration changed. In other words, the pseudo T-T-T curve for the usual water quenching is a C-curve having a nose near 700°C, independently of the amount of concentration.

In the following,we show examples of the structures corresponding to different thermal treatment. Photos 1(a)-(c) show the structures after isothermal treatment in high concentration alloy. In the neighborhood of the nose at around 500°C in the low temperature side, the precipitates are extremely fine as seen in (a) and rather dense and uniformly distributed. However, near the valley, 650°C, of the curve, the distribution is rather thin as shown in (b) and near the nose, 800°C, of the high temperature region, the

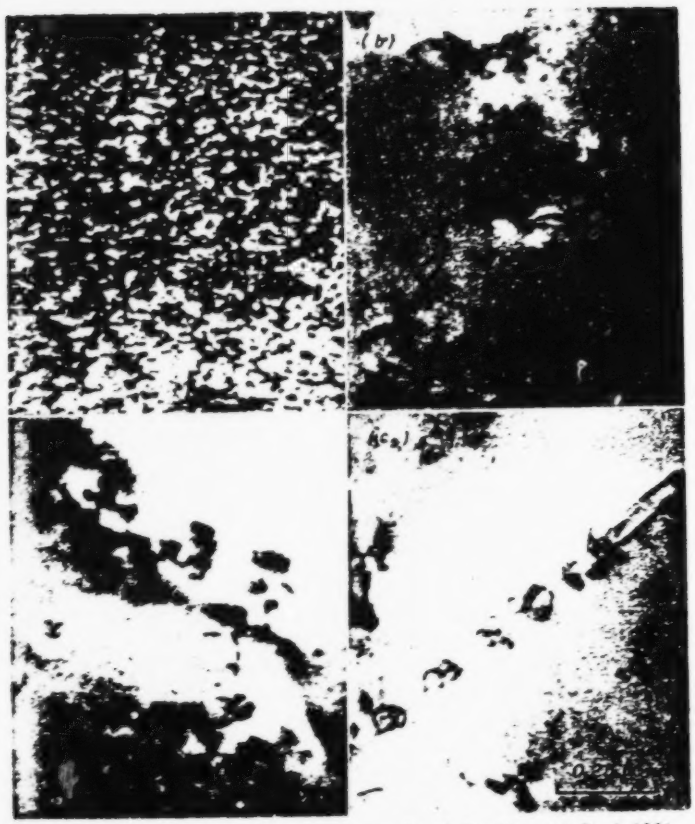


Photo.1 Transmission electron micrographs of directly aged Cu-1.16% Cr alloy. Specimens were solution-treated at 1000 C for 30 min and subsequently directly aged at 500 C for 1000 sec (a), at 650 C for 1000 sec (b), and at 800 C for 100 sec (c_1, c_2)

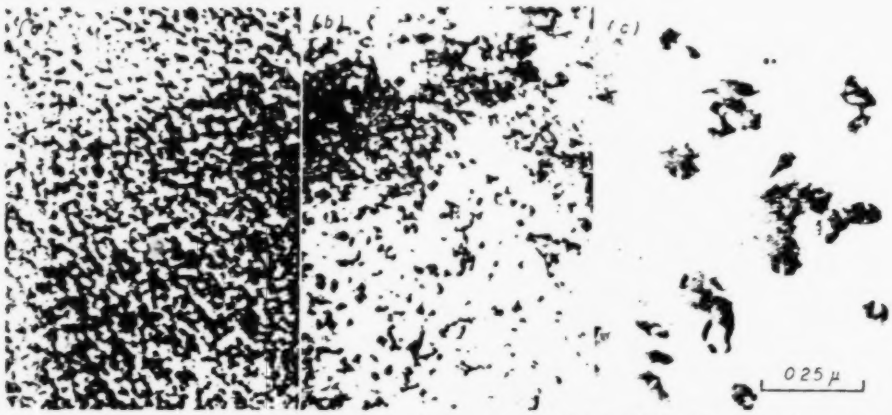


Photo.2 Transmission electron micrographs of normally aged Cu-1.16% Cr alloy. Specimens were solution-treated, quenched into water and subsequently aged at 500 C for 1000 sec (a), at 700 C for 100 sec (b) and at 800 C for 100 sec (c)

distribution is very inhomogeneous, and most of the precipitation occurs on dislocation borders and grain boundaries.

On the other hand, photos 2(a)-(c) show the cases where aging was done after the conventional water quenching. In this case of (a) 500°C aging, fine precipitates distrigute uniformly and the situation is almost the same as the previous isothermal treatment case. At 700°C (b), which corresponds to the nose of the C-curve, the distribution slightly thins, but still is uniform, and precipitation on dislocation borders is not observable. Further, at 800°C (c), the precipitates increase in size but the distribution is still uniform.

IV. Discussion

In the above observation of the structures, near the low temperature side nose in isothermal treatment and near the nose in aging after water quenching, precipitates are distributed densely and uniformly. However, generally speaking, ideal uniform distributions do not occur even in such cases, and it is expected that precipitation occurs primarily at some lattice defects [11]*. Among various defects such as grain boundaries, dislocations, residual Cr grains, oxidized particles and assemblies of cavities, only assemblies of cavities will probably produce an apparently uniform distribution of precipitates. (In the nucleus action of assemblies of cavities, their thermal stability must be considered. However, in pure Cu, they are stable even after thermal treatment of 490° x 1 hr).

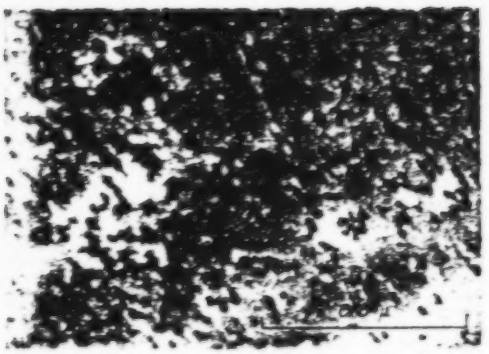
*Differing from the alloy group of the G.P. formation type which is considered to form ideally homogeneous nucleus formation; for Cu-Cr alloy, since not being the G.P. formation type, we considered the nucleation by cavity assemblies as in the case of Al-Si alloy [13] (in the case of high temperature aging where G.P. is not formed even for the alloy of the G.P. formation type). By this theory, the experimental results given below are easily explained.

We first examine the uniform precipitation in the above described sense and then study the T-T-T curve of the C-shape which we are concerned with. Table 1 shows results of changes in the amount of precipitates by simple aging or step-wise aging in high concentration alloy. From the table, we see that if we age (500°C x 1000 sec) at the temperature of the low temperature nose after holding for a predetermined time (700°C x 100 sec) after quenching at the temperature region where precipitation is extremely slow, following solution treatment, the amount of precipitates is considerably less compared to the case where direct aging of 500°C x 1000 sec was applied. The corresponding structure is shown in photo 3. Compared to photo 1(a) of 500°C x 1000 sec, the precipitates are slightly bigger in size and distribution is rather thin. This is probably because the cavity concentration was decreased in the first step thermal treatment, the number of nuclei decreased in the second step and consequently, the amount of uniformly distributed precipitates decreased.

Table 1 Effects of direct or step-wise aging on the amount of precipitates, i.e., the conductivity of alloy Cu-1.10% Cr specimens, cold

Aging condition	I.A.C.S %
700°C x 100 sec	41.5
500°C x 1000 sec	78.2
700°C x 100 sec + 500°C x 1000 sec	69.1
500°C x 10 sec	39.9
500°C x 100 sec	59.8
500°C x 10 sec + 500°C x 100 sec	70.6

Next, we quench and hold at a low temperature (500°C x 10 sec) (we do not observe changes in specific resistant at this point) and then hold at the temperature of the high temperature nose (800°C x 100 sec). Then precipitation is accelerated compared to the case where aging was done at 800°C x 100 sec from the beginning. An example of the corresponding structure is shown in photo 4, which is quite different from photo 1(c_1). Together with innomogeneous precipitation on the dislocation boundaries, we also clearly observe precipitates B which must have precipitated inside. The precipitate B is probably nucleated by assemblies of cavities at 800°C which were formed at 500°C by quenching. Although we made this simple statement, the real question is when the assemblies of cavities were formed. It is not clear whether they were formed during quenching.



in the 10 sec holding time, in the process of raising the temperature or in all of these processes. Also, even if we assume that the assemblies of cavities were formed by some kind of processing, it is conceivable that they might disappear in the process of raising the temperature or aging at 800°C. In such a case, both the disappearance rate and the precipitation rate of the solvent influence the situation. However, unless the size of the assemblies is known, they cannot be determined. If the assemblies remain at the beginning of 800°C aging, they will, of course, nucleate. Also, if some solvent is precipitated before the assemblies reached 800°C, they are stabilized and possibly nucleate. In conclusion, the above questions remain about precipitate B. However, in principle, if conditions are satisfied so that the assemblies of cavities do not disappear even at the temperature of the high temperature nose, then it is likely that precipitates distribute evenly. The reason for that the structure (photo 1 (c_1)) of 800°C direct aging in the present experiment showed inhomogeneous distribution is probably that at this temperature, the assemblies were not formed. In the case of aging after water quenching, the aging temperature of the first step of the aging corresponds to an extremely low temperature case. Therefore, because of the reasons described earlier, uniform distribution was maintained even after a relatively high temperature aging, and precipitation was accelerated.

Next, we discuss the shape of the T-T-T curve. Generally speaking, the curve is of the C-shape, which is established in the classical theory of uniform nucleus formation [15]. In the case of inhomogeneous distribution, if we expand the theory [16], a C-curve is created at each temperature of inhomogeneous nucleus formation and consequently, many noses will appear. Namely, in

isothermal treatment, the nose due to uniform precipitation nucleated by the assemblies of cavities in the low temperature region appears, and in the high temperature region, the nose due to inhomogeneous precipitation at dislocation lines and grain boundaries appears and uniform precipitation is prevented. This was confirmed by actual observation. However, the number of the nose at the high temperature side will be more than one, if by increasing accuracy of the measurement and narrowing the interval of the temperature, we can separate each inhomogeneous precipitation. On the other hand, in water quenching, it may be the case that by extending the nose of the homogeneous precipitation to the high temperature region (described earlier), other inhomogeneous precipitations were prevented or even if the latter occurred, the uniform precipitation dominated and resulted in producing the C-curve with a single nose.

Effects of the amounts of Cr on the T-T-T curve do not have many questions. In the low concentration alloy, precipitation was slower and the amount was considerably smaller, compared to the intermediate and high concentration. This is clear because the degree of supersaturation (the limit of solid solution at the solution temperature is about 0.4%) and the free energy of nucleus formation is large. The high temperature nose is more pronounced as the amount of Cr increases. This can be explained as follows. For example, in intermediate and high concentration alloy, the amounts of dispersed Cr particles (average grain size 1 μ) remained during and after the solid solution process are different. The dispersed particles, of course, reduce the size of the crystals, increase the concentration of grain boundaries and create a pressure on the surrounding during a rapid cooling, and tend to cause dislocations. Also, the dispersed particles themselves nucleate inhomogeneous precipitation. All these accelerate inhomogeneous precipitation which causes the high temperature side nose. On the other hand, an increase of concentration of the grain boundaries by Cr particles makes disappearance of cavities easier. Therefore, we expect that in the beginning of low temperature aging,

precipitation is slightly slower in high concentration than in low concentration. Experimental results confirmed this.

Lastly, we describe the quenching characteristics of Cr-Cu alloy. Although the low temperature side nose is not affect, if the temperature is in the high temperature side nose region, inhomogeneous precipitation was observed in thick specimens, and the amount of precipitates in the subsequent aging treatment decreased. Also, it is natural that inhomogeneous precipitation occurs and the quality becomes inferior. These phenomena are expected to be in common in Cu-Co alloy which is believed to be of the homogeneous precipitation type.

V. Conclusion

(1) In the past, Cr-Cu alloy was believed to be of the homogeneous precipitation type. However, we found that considerably inhomogeneous precipitation occurred, depending on different thermal treatments. (2) We confirmed by structure observation that of the two noses of the ε-type -T-T curves, the low temperature side nose is created by the so-called homogeneous precipitation and the high temperature side nose by inhomogeneous precipitatiyn at grain boundaries. (3) If aging after the conventional water quenching is done, homogeneous precipitation is observed even if aging is done at a high temperature, probably because a large number of cavity assemblies are stabilized. The low temperature side nose shifts towards the high temperature side and as the result, the T-T-T curve appears to be the C-curve. (4) The T-T-T curve for alloy of the simple precipitation type (a single phase in precipitation) such as Cr-Cu alloy, it is usually believed that the T-T-T curve is the C-curve. However, from the results of the present study, the ε-type appears more natural to be expected. (It is well known that the curves is of the ε-type or the plural nose type for alloys of the non-simple precipitation type). (5) The reason for problems in the quenching characteristics of Cr-Cu alloy is that the high temperature side nose in the alloy of

commonly used concentration happens to be located at the short elapsed time position.

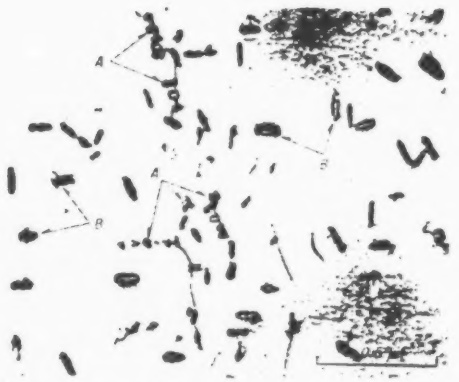


Photo. 4 Transmission electron micrograph of step-aged Cu-1.16% Cr alloy. Specimen was solution treated, directly aged at 500 C for 10 sec and finally aged at 800 C for 100 sec (Arrow A indicates precipitate nucleated and grew on or along dislocation lines at 800 C; B indicates precipitate nucleated at 500 C and grew at 800 C.

REFERENCES

[1] W. Koester and W. Knorr: Z. Metallk., 45(1954), 350.

[2] W. Gruehl and W. Fisher: Z. Metallk., 46(1955), 742.

[3] Dai, Journal of the Metallurgical Society, 21(1957), 337, 720.

[4] R. O. Williams: Trans. ASM, 52(1960), 530.

[5] Nishikawa, Nagata, Kobayashi. J. of Metall. Soc. 30(1966),302

[6] Nishikawa, Nagata, Kobayashi. " 30(1966),760

[7] Suzuki, Kitano, Kanno, " 33(1969),334

[8] Suzuki, Kanno, Kawakatsu " 33(1969),628

[9] Toda: " 29(1965),238

[10] Sato, Nagata: " 33(1969),,55

[11] for example, V. W. Christian: The Theory of Transformation in Metals & Alloys, Pergammon Press (1965), p. 377.

[12] L. M. Clarebrough, P. Humble, M. H. Loretto: Acta Met. 15(1967), 1007.

[13] H. S. Rosenbaum, D. Turnbull: Acta Met., 6 (1958), 653.

[14] Kimura: Aging Process and Explanations in Alloy (Japanese Metallurgical Society), (1968), p. 70.

[15] for example, J. H. Brophy, R. M. Rose, J. Wulff: Thermodynamics of Structure, John Wiley & Sons (1964), p. 104.

[16] M. F. Fine: Phase Transformation in Condensed Systems, (1964), p. 43.